

**INTEGRATED RAMAN-pOH SENSOR FOR  
IN-TANK CORROSION MONITORING**

**RAMAN FEASIBILITY STUDY REPORT**

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**by**

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## INTRODUCTION

This project addresses the need to monitor species related to corrosion in high-level liquid waste tanks at the Savannah River Site (SRS). Ultimately, the method will be applicable at Hanford and other DOE facilities. A primary source of corrosion is the nitrate ion, often present at high concentrations in the tanks, but which can be controlled (inhibited) by maintaining adequate levels of hydroxide and nitrite ions. The ideal sensor for this application is one that accurately and safely monitors all three anions directly in the tank liquid, eliminating the need for traditional grab sampling and analysis.

We have identified fiber optic Raman spectroscopy as a leading candidate for simultaneous, in-tank monitoring of nitrate, nitrite, and hydroxide. Raman spectroscopy is an optical technique that produces a unique "fingerprint" spectrum for every molecule. Its spectral features are sharp, so multiple components of mixtures can often be differentiated without physically separating them. Although a full Raman instrument is unsuitable for in-tank deployment, small, flexible fiber optic probes connected to the instrument can be readily delivered into the tanks for *in situ* monitoring.

The objective of the first, 6-month phase of this program was to establish the feasibility for Raman detection of nitrate, nitrite, and hydroxide at concentrations relevant to hazardous waste tanks. Specific tasks were to:

1. Establish minimum detectable concentrations and linear dynamic range for nitrate, nitrite, and hydroxide, as well as other potentially interfering anions in aqueous solutions.
2. Determine the effect of optical fiber length (up to 100ft.) on Raman sensitivity.
3. Evaluate potential interference (from other anions) to the detection of nitrate, nitrite, and hydroxide through the analysis of mixtures, including formulations similar in composition to real waste tank contents at SRS.

This report presents the results of our tests, which demonstrate that Raman monitoring of nitrate, nitrite, and hydroxide at relevant waste tank concentrations is feasible.

## EXPERIMENTAL SECTION

The Raman experimental configuration used for the feasibility study is shown in Figure 1. The major components of the system are a laser for excitation, a spectrograph which disperses and detects the Raman spectrum, and a fiber optic probe that delivers laser light to the sample and delivers Raman scattered light collected by the probe to the spectrograph. In the course of our work, krypton ion (647nm, 676nm - Coherent) and diode laser (785nm - Spectra Diode Laboratories) sources were employed. Two spectrographs, an EIC near-IR, fixed echelle grating spectrograph aligned and calibrated for operation with 785nm excitation, and a SPEX-ISA 270M

spectrograph with a movable grating, were used to disperse the Raman spectra. Both spectrographs were outfitted with multichannel CCD camera detectors produced by Photometrics, Ltd.

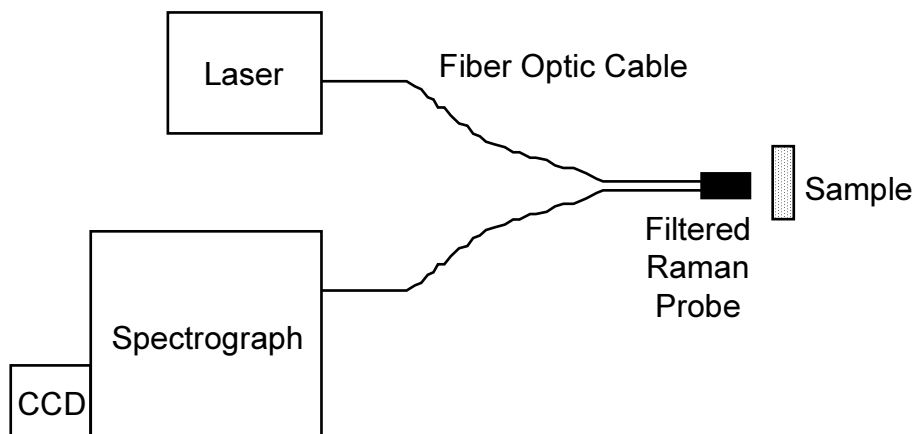


Figure 1. Raman experimental configuration.

A different fiber optic Raman probe was used at each operating wavelength because wavelength-specific filters are employed in them to reduce Raman and fluorescence background generated in the optical fibers. However, all of the probes had the basic configuration shown in Figure 2. The geometry of the probe is  $180^\circ$  backscattering where excitation and collection take place through a common front lens. This is an efficient geometry and one which is used in most commercial Raman systems. As long as the laser beam is focused well into the sample liquid, slight changes in positioning of the probe have little effect on the measured Raman intensity. Key components in the probe are a bandpass filter which passes only the desired laser wavelength, a dichroic filter which acts as a beamsplitter, and a longpass filter which passes the Raman scattered light while blocking specular and Rayleigh scattered light at the laser wavelength.

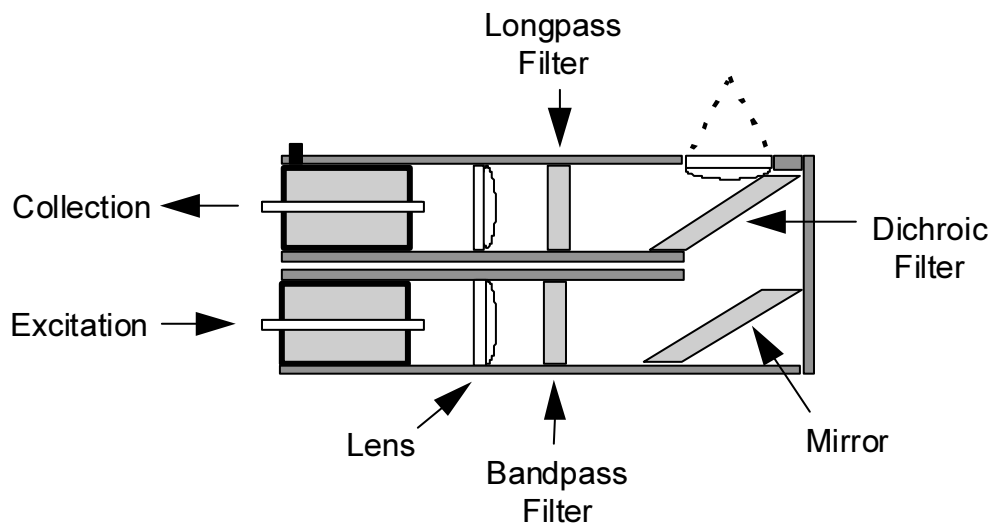


Figure 2. Fiber optic Raman probe.

The Raman probe was connected to the laser and spectrograph with a bifurcated fiber optic cable consisting of 100 $\mu$ m core excitation and 200 $\mu$ m core collection fibers. The fibers were of high purity, all-silica construction. Different lengths of cable up to 100ft were tested to determine the effect of fiber length on the measured Raman spectrum.

## RESULTS AND DISCUSSION

### Preliminary Considerations and Effect of Fiber Length

The Raman band for hydroxide is located far out in the spectrum (near 3600 $\text{cm}^{-1}$ ). In preliminary experiments we found that hydroxide could not be detected sensitively with 785nm excitation because the band was located at 1.1 $\mu$ m, which is at the upper wavelength limit of CCD detectors. Therefore, we used 647nm or 676nm excitation for all subsequent work. There was little difference in the results obtained at either of these red wavelengths.

Samples of several individual anions were used to test the effect of fiber length on the Raman spectrum. There was no significant difference in the results for different anions. The only effect of increasing fiber length was a decrease in the measured Raman signal intensity. Because optical filters were used in the Raman probes, there was no increase in the spectral background observed from the fibers when long fibers were tested.

A typical result for 0.1M sulfate is shown in Figure 3. In going from a 16ft cable to a 100ft cable, the Raman signal intensity decreased to 40% of its original level. This can be attributed solely to the optical attenuation of the fibers, which increases with fiber length. We measured the optical transmission through both the excitation and collection cables and found that it was 70% and 59%, respectively, in going from the 16ft to the 100ft cable. The excitation fiber transmission was measured at the laser wavelength and the collection fiber transmission was measured at the sulfate band position (983 $\text{cm}^{-1}$ ) - when measured at the same wavelength, the excitation and collection fiber transmissions were equal, as expected. The measured transmissions were also consistent with the manufacturer's "typical" specifications. Based on the combined excitation and collection fiber attenuations, the calculated Raman intensity decrease when going from the short to the long fiber was 59%, which agrees well with the 60% measured decrease.

Clearly, the use of shorter optical fibers is advantageous from the standpoint of sensitivity. However, even with a 100ft length of cable (which should be wholly adequate for this application) the modest loss in sensitivity can be recovered by increasing the measurement time. Typically, we found that increasing the maximum detector integration period for low concentration samples from 1-2 minutes to up to 5 minutes was sufficient to maintain a comparable signal-to-noise level with the long fiber for all the anions tested. This increased integration period is insignificant when compared to many other more time-consuming steps in the tank monitoring process (e.g., instrument transport and setup).

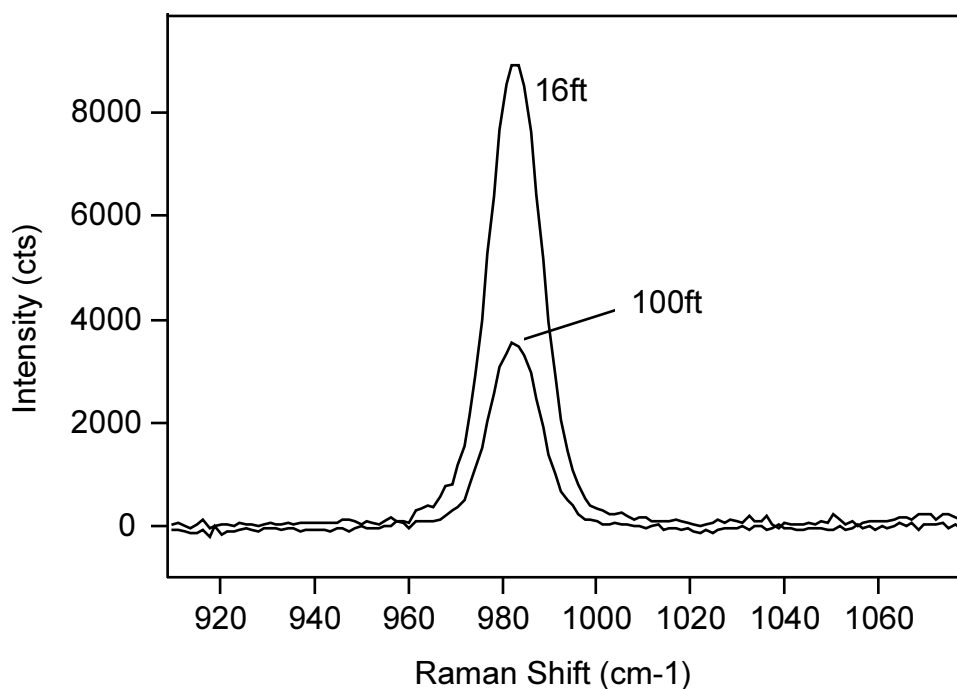


Figure 3. Raman spectrum for sulfate collected through different lengths of optical fiber.

### Individual Anion Testing

A second set of experiments was performed with a series of individual anions (nitrate, nitrite, hydroxide, and potential interferents) prepared as aqueous solutions at varying concentrations. Analytical figures of merit including linearity of Raman response vs. concentration and minimum detectable concentrations were determined for each anion using the 100ft fiber optic cable and 30mW of 676nm excitation at the sample. The results are presented in Table 1.

Table 1. Analytical Figures of Merit for Individual Anions

<i>Anion</i>	<i>Target (M)</i>	<i>LOD (M)</i>	<i>Linearity (<math>r^2</math>)</i>
Nitrate	0.02 - 3.2	0.004	0.999
Nitrite	0.05 - 3.0	0.02	0.997
Hydroxide	0.03 - 13.4	0.05	0.999
Aluminate	0.01 - 1.1	0.01	1.000
Carbonate	0.01 - 1.0	0.01	0.996
Sulfate	0.001 - 0.4	0.0006	0.998
Phosphate	0.001 - 0.06	0.0007	0.996
Chromate	0.001 - 0.05	0.008	1.000
Silicate	0.001 - 0.05	0.007	0.998
Oxalate	0.001 - 0.01	0.007	0.996

In the table, the "Target" concentration ranges are those found across the SRS Tank Farm. For nitrite and hydroxide, these ranges have higher minimum levels than those originally targeted for this program (0.01-10M hydroxide; 0.005-5.5M nitrite; 0.1-5M nitrate). For each ion, we were able to easily measure the highest concentration in the target range. With nitrate and nitrite we determined linearity from 5M to the lower limit of detection (LOD). For hydroxide the maximum concentration was 10M. Linearity for potentially interfering anions was determined from near the upper solubility limit to the LOD. With the exception of (sodium) aluminate, the upper solubility limit was always well above the upper target concentration.

Of the three primary anions of interest, both nitrate and nitrite were detectable at concentrations below those found in the SRS Tank Farm, and hydroxide was detected very near the lower SRS limit (0.05M vs. 0.03M SRS lower limit). Most other anions were detectable at concentrations relevant for in-tank monitoring, although that is not the focus of this investigation. In all cases, the linearity of response was excellent, indicating that without spectral interference quantification is feasible and straightforward. Linear correlation coefficients for nitrate, nitrite, and hydroxide were 0.999, 0.997, and 0.999, respectively.

The reproducibility of the Raman measurements was also excellent. In a series of experiments, the Raman spectrum of a nitrate/nitrite/sulfate mixture was divided into six aliquots which were measured independently at different times in the course of a day. The mean of the six measurements was 3254 counts for the  $1050\text{cm}^{-1}$  nitrate ion peak, with a standard deviation of just 19 counts.

The highly alkaline pH of the high-level waste tanks, and certainly those where hydroxide is being used to control corrosion, means that most of the anions in this study will be analyzed in their fully ionized states. Phosphate, however, could be present in either or both of its tribasic or dibasic forms in the tanks. Raman spectra for phosphate at three different pH values are presented in Figure 4. At pH 13, the spectrum is predominantly that of  $\text{PO}_4^{3-}$  with a characteristic band at  $936\text{cm}^{-1}$ . Lowering the pH to 11, where the major phosphate species is  $\text{HPO}_4^{2-}$ , produces a very different spectrum with the strongest band at  $990\text{cm}^{-1}$ . At pH 6, below the pH of the tanks, bands at  $878\text{cm}^{-1}$  and  $1077\text{cm}^{-1}$  are observed for  $\text{H}_2\text{PO}_4^-$ . Thus, the major phosphate bands to be concerned with as potential interferences are at  $936\text{cm}^{-1}$  and  $990\text{cm}^{-1}$ .

### Potential for Spectral Interference

An important consideration when measuring nitrate, nitrite, and hydroxide in real tanks is the potential for Raman bands from other anions to overlap the analytical bands of interest. Raman spectra for all of the anions tested are presented in Figures 4-7. The hydroxide band at  $3612\text{cm}^{-1}$  (see Figure 5) is completely isolated from the other oxyanions and interference from them is not a concern, but sensitivity is limited by a broad, overlapping water band. Nitrite, with a strong band at  $1333\text{cm}^{-1}$ , is also spectrally well resolved from the other anions with the exception of oxalate, with bands at  $1311\text{cm}^{-1}$  and  $1488\text{cm}^{-1}$ . As indicated in Table 1, however, the lowest nitrite concentration in the tanks is five-fold higher than the highest oxalate concentration. With the oxalate band at  $1311\text{cm}^{-1}$  having a Raman scattering cross-section about half that of the

nitrite band and only partial overlap of spectral bands (see Figure 8), oxalate will not interfere significantly with nitrite quantification in the SRS tanks.

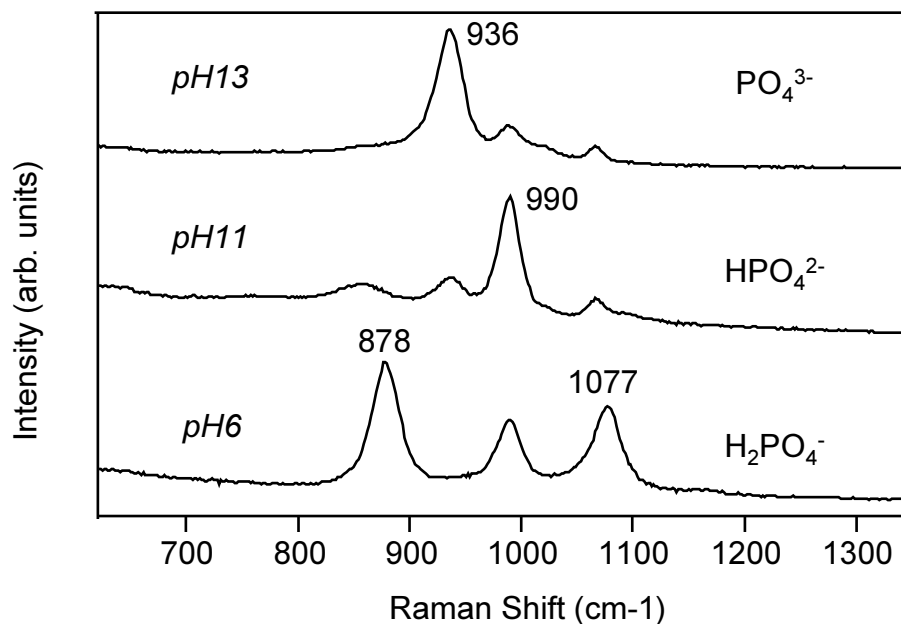


Figure 4. Raman spectra for phosphate at three different pH values.

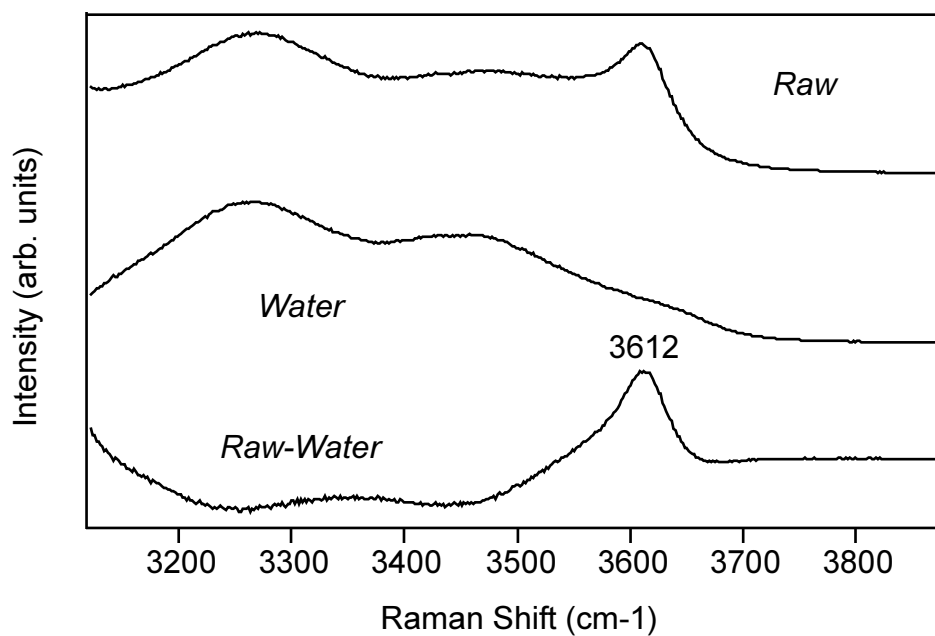


Figure 5. Raman spectrum of the aqueous hydroxide ion.

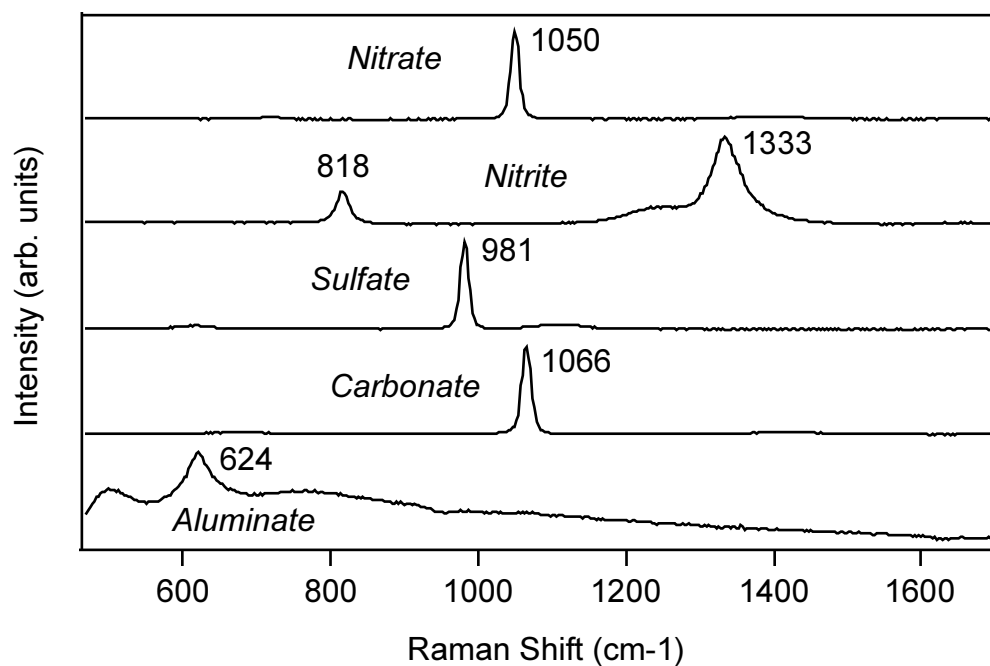


Figure 6. Raman spectra of aqueous anions found in high-level waste tanks.

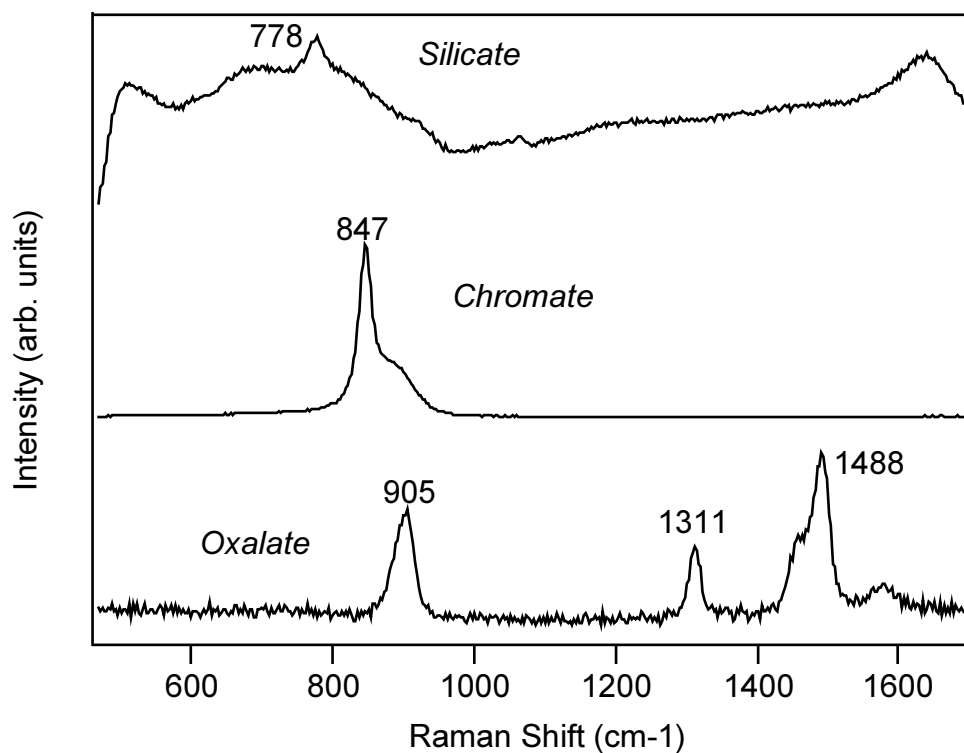


Figure 7. Raman spectra of additional aqueous anions found in high-level waste tanks.



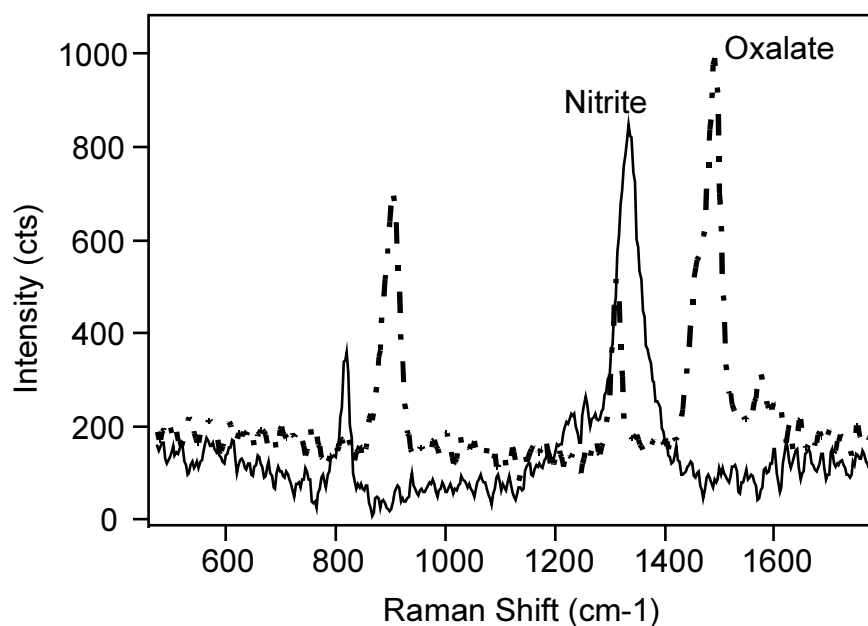


Figure 8. Raman spectra of nitrite and oxalate at equal aqueous concentrations.

In the case of nitrate with a major band at  $1050\text{cm}^{-1}$ , there is a potential for greater interference from carbonate at  $1066\text{cm}^{-1}$ . The natural linewidths of the anions set the minimum spectral bandwidth to about  $10\text{cm}^{-1}$  (full width at half maximum), which means that there is substantial overlap between the two peaks, as shown in Figure 9. As shown in the figure, dibasic phosphate could also pose an interference although the overlapping band is a minor one in the phosphate spectrum. Considering again the concentration ranges found in the SRS tanks (see Table 1), the concentration of phosphate could be as much as three fold higher and carbonate as much as 50 fold higher than nitrate. The relative Raman scattering cross-sections for the 3 overlapping bands are 24 (nitrate):10 (carbonate) : 1(phosphate). Therefore, we conclude that phosphate will not interfere with the determination of nitrate in the SRS tanks. In tanks where carbonate is present at 20-fold or higher concentration than nitrate, the quantification of nitrate will be difficult. However, the likelihood that nitrate will pose a significant corrosion hazard in those tanks is small since the nitrate concentration will have to be low to allow for such a large overconcentration of carbonate.

### Anion Mixtures Testing

In order to further establish that quantification of nitrate, nitrite, and hydroxide is feasible in waste tanks, a series of anion mixtures were prepared and analyzed “blind” by the staff scientist on this project. The samples ranged from simple two-component mixtures to a complex simulant for an SRS tank. For all of the mixtures, quantification was highly accurate and comparable to that noted previously for the individual ions.

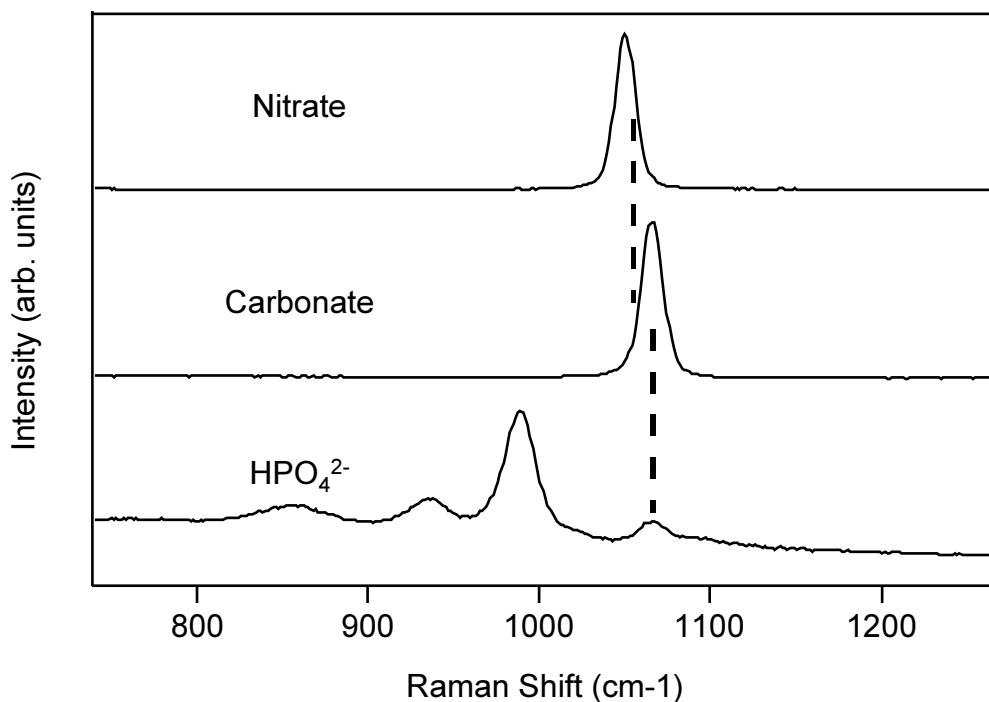


Figure 9. Potential interference to the quantification of nitrate from carbonate and  $\text{HPO}_4^{2-}$ .

The most challenging of the mixtures tested was the SRS waste tank simulant. The "oxyanion" Raman spectrum for the simulant is shown in Figure 10. Strong bands for nitrate ( $1050\text{cm}^{-1}$ ) and nitrite ( $818\text{cm}^{-1}$  and  $1333\text{cm}^{-1}$ ) are readily apparent in the spectrum, along with a number of weaker bands. A closer view of the spectrum near baseline (Figure 11) shows that aluminate, phosphate ( $\text{PO}_4^{3-}$ ), and sulfate were present in the sample. Hydroxide was readily detected in the sample as shown in Figure 12.

Quantification was performed for nitrate, nitrite, and hydroxide in the simulant mixture. The results are presented in Table 2. The agreement between the prepared and measured concentrations of nitrate, nitrite, and hydroxide was excellent. There was a greater variance observed for the other anions which in many cases were present near their lower limit of detection. Phosphate was present as  $\text{PO}_4^{3-}$  at the detection limit and oxalate went undetected because it was present below its lower detection limit. Being an atomic species, chloride is not Raman active and is undetectable. Although carbonate was present at a concentration above its detection limit, it could not be quantified due to overlap from the intense nitrate band. The measured concentration for aluminate was low, which we attribute to the sparing solubility of the aluminum salt used to prepare the simulant (there was a small quantity of undissolved solid in the sample and the aluminate salt was the least soluble material used to prepare the sample).

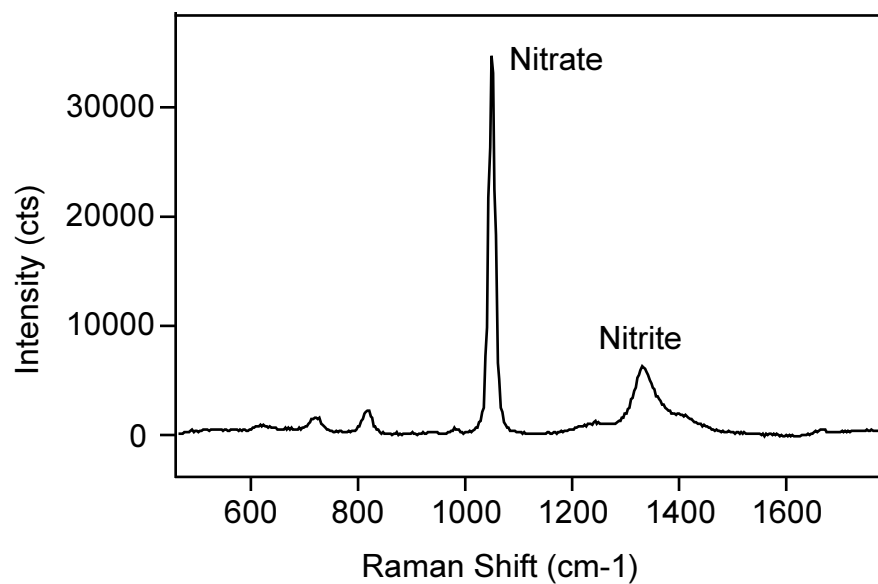


Figure 10. Raman spectrum of SRS waste tank simulant - oxyanion region.

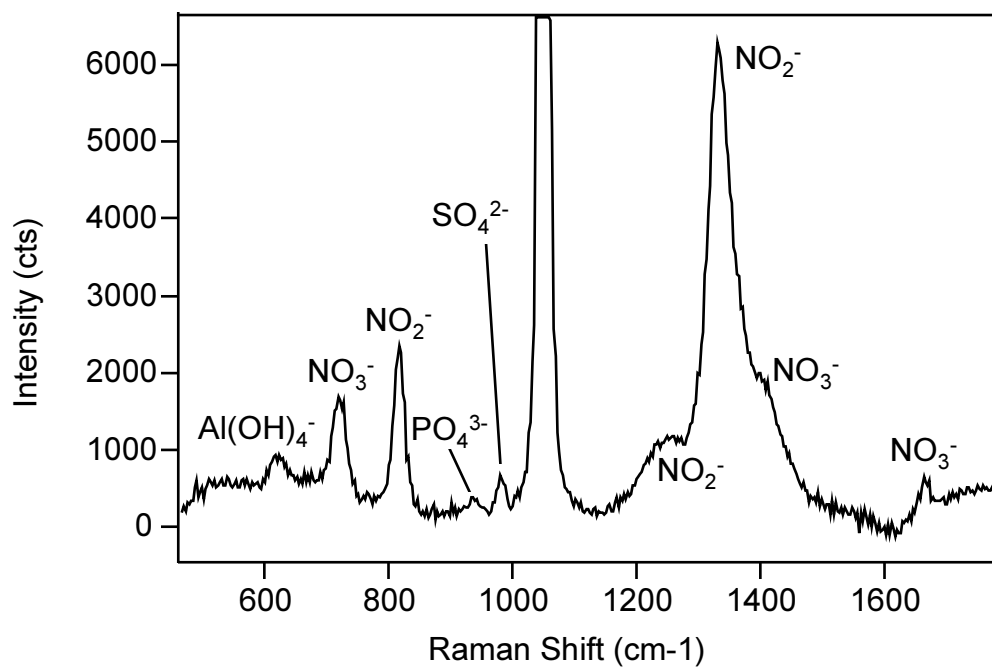


Figure 11. Near-baseline view of minor constituents shown in Figure 10.

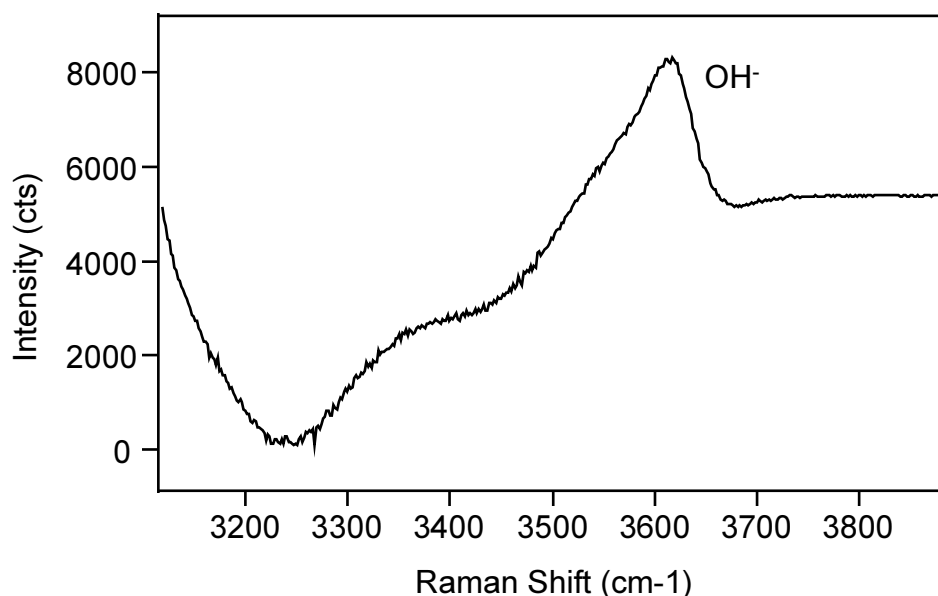


Figure 12. Raman spectrum of SRS waste tank simulant - hydroxide region.

Table 2. Quantification of key anions in the waste tank simulant

<i>Anion</i>	<i>Prepared (M)</i>	<i>Measured (M)</i>	<i>LOD (M)</i>
Nitrate	1.1	1.0	0.004
Nitrite	1.0	1.0	0.02
Hydroxide	3.85	3.6	0.05
Sulfate	0.010	0.008	0.003
Phosphate	0.014	0.02	0.02
Aluminate	0.10	0.03	0.01
Carbonate	0.020	Not detected	0.008
Oxalate	0.010	Not detected	0.02
Chloride	0.008	Not detected	Not detected

## CONCLUSIONS

The feasibility for using fiber optic Raman spectroscopy to monitor nitrate, nitrite, and hydroxide ions at concentrations relevant to those found in corrosion controlled hazardous waste tanks at SRS has been demonstrated. Lower concentration limits for detection of nitrate and nitrite over a 100ft fiber optic cable were below the range found in the tanks and strong Raman signals were observed at concentrations that are typical of tanks in which corrosion control is being conducted. The minimum detectable concentration of 0.05M determined for hydroxide was slightly above that found in the lowest of the SRS tanks (0.03M), but was again well below the levels used to inhibit corrosion (typically over 1M). The Raman response of individual species was shown to be linear with concentration and measurement reproducibility was within 1%.

Other anions commonly present in waste tanks were studied individually and in mixtures to identify possible interference to the quantification of nitrate, nitrite, and hydroxide. No interference was observed for the strongest nitrite and hydroxide bands. For the predominant nitrate band, a partial overlap with the strongest carbonate band was observed. It was determined that in tanks where carbonate is present at 20-fold or more of the nitrate concentration, nitrate quantification would be exceedingly difficult. However, based on the levels of carbonate found in the tanks (1M maximum), this scenario requires that the nitrate concentration be very low (0.04M), posing a correspondingly low corrosion hazard. This level of nitrate is much lower than that typical of tanks for which corrosion control is practiced and is near the lowest levels found at SRS (0.02M).

In a final test, nitrate, nitrite, and hydroxide were quantified at typical concentrations in a waste tank simulant matrix. The measured concentrations agreed well with the prepared concentrations and no spectral interferences were observed. Having successfully demonstrated feasibility, this project is expected to move to the next phase which is to develop an in-tank sampling design suitable for deployment in an SRS tank. We plan to collaborate with SRS and Applied Research Associates (ARA) in the design. ARA is an engineering company with considerable experience and commercial products in the area of remote liquid sampling in turbid media (e.g., tank sludge, mud, etc).